

THE ADDITION OF ALCOHOLS AND
PHENOLS TO FLUOROLEFINS

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SUMMARY

The work described in this dissertation was performed under the sponsorship of the Office of Naval Research.

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CHAPTER I

INTRODUCTION

This work describes the base catalyzed addition of organic compounds having a hydroxyl group to fluorocarbon chains, or "fluorofunctions", as they are designated for brevity in this document. This reaction is occurring from a number of viewpoints: the addition is not random and offers a number of theoretical possibilities; several uses for the products have been proposed and the stereo formed are useful parameters for the properties of various compounds exhibiting fluorine.

The addition of alcohols or phenols to olefins is the process of a basic catalyst to an example of a non-polarizable attack on the carbon-carbon double bond, and as such, contrasts to the ordinary additions to olefins that are catalyzed by acids and therefore initiated by an electrophilic attack of the hydrogen ion or some other electrophilic species. These two types of addition may be illustrated by the following equations of well known addition to the pentene-carbon double bonds:

^aNon-polarizable here is used to denote that a non-polarizable reagent is one that does not, or cannot, ionize, with no electron deficient reaction center.

I. Electrophilic attack



II. Nucleophilic attack



It can be seen that in I the initial attack is illustrated at the chlorine rich carbon atom and therefore factors that enhance this contribution, such as the inductive or polarizing effect of substituents promote this reaction. In II the attack is by the negative ion and it uses the chlorine deficient atom as a reaction center, therefore factors decreasing the chlorine density at a given carbon atom favor the development of a nucleophilic reagent. The reaction shown is the type known as epoxidation, and is considered a typical type of the second mechanism, whereas nucleophilic reagents add to the double bond of a π_2 system to form a three carbon chain. The epoxide group arises from the polarization of the carbon-carbon double bond so that the carbon's oxygen is a nucleophilic reagent.



In general, it has been found that atoms having the fluorine atom attached to one surface undergo antiperiplanar addition to the surface to which the fluorine are attached. It must therefore be assumed that the effect of the fluorine is to decrease the availability of electrons around the surface to which they are attached so that on such a surface such atoms must be relatively positively charged. This final effect might be due to a number of operational causes. The relative electronegativity or the electron attracting properties of the halogen, particularly fluorine, is well recognized, as is an effect operating in the opposite direction, that of the tendency for the numbered electrons of the halogen to contribute to partial double bond character of the carbon-halogen bond in response structures. This second effect, though probably to explain the very dimming influence of halogen attached to a benzene ring, is not necessarily definitely operative in the present case, nor is the concept of polarization of the bonds used by the definitive effect of the halogen. It seems reasonable, rather, that the fluorine atom by depriving the electrons directly about the carbon is

The quantitated amounts and their activation or deactivation agrees with the approach of the negatively charged addition.

The stimulative and activating effects upon ring II additions to the chlorophylls are certainly not so easily stated as the β -activation of the cationic ion by the simple electron-shifting proposed for the Michaeli reaction. Also, the effects of these effects will be complicated by the presence of other polar substituents on the series other than those having the fluorine atoms. Abilities of an alcohol to deactivations can, of course, give only one final resulting product. Therefore, for the purpose of this investigation, three monoalkylallyl substituted chlorophylls, chlorophyll, chlorophyll and chlorophyll were selected. These actions will give structurally homologous changes depending on the dimension of addition.

Variations in the structures of the adducts should also exert an appreciable influence on the course of a reaction of this type. With this in mind, a series of the lower alcohols with decreasingly branched structures, methyl, ethyl, isopropyl, isobutyl, tert-butyl, etc., etc., etc.

This extension of research should give a picture of the associative relationship of fluorine and chlorine and the solvating and weakening of the resulting products should help to clarify the normal and anomalous quite unexpected properties fluorine imparts to otherwise normal and well-known organic structures.

While with a consideration of this research, some mention

may be made of the possible uses of the compound produced. Miller and Scott have suggested the other five addition of the chlorine to heat sensitive flights, starches etc; the two chlorine types may find uses as disinfectants or as additives for insecticides. The eight others have been used as valuable intermediates for preparation of a wide variety of fluorine compounds, particularly the derivatives of fluorophenoxoacetic acid. Although no medicinal, insecticidal and bactericidal properties of these compounds have not been reported, some of their properties, for instance, the enhanced sensitivity of chlorine atoms attached to an ether linkage, would warrant further investigation.

CHAPTER II

PREPARATION OF MATERIALS

The fluorotitanates were made by dehalogenation of the corresponding activated esterified epoxides.

Titaniumchloride, $\text{Cl}_2\text{Ti} \approx 99\%$, was obtained by dehalogenation of 1,1,2-trichloro-1,2,2-trifluorotitanane, from KU, supplied by Electro Metallics Co. The esterite was well-diluted before use.

2,2-DIFLUORO-2-VINYLCHLORIDE, $\text{Cl}_2\text{C}_2\text{F}_2 \approx 99\%$, was prepared by two methods: 1) dehalogenation with 10% zinc of a 2,2-DIFLUORO-1,1,2,2-tetrachloroethane, Eastman 10%, supplied by General Chemical Company and 2) by thermal dehydrochlorination of 2,2-DIFLUORO-1,2,2-trifluorotitanane, a product of the fluorination of propylchlorotitanane by activated trifluorotitanane. Method (2) is described by Borkin⁷. Esterite prepared by the latter method was washed free of dissolved hydrogen chloride and distilled before use.

2,1-DIFLUORO-2-VINYLCHLORIDE, $\text{Cl}_2\text{C}_2\text{F}_2 \approx 99\%$, was prepared by dehalogenation with zinc of 2,2-DIFLUORO-1,1,2,2-trifluorotitanane prepared by fluorination of propylchlorotitanane with activated trifluorotitanane.

Bis(ethyl, vinyl and allyl)benzene monomers were from various laboratory supplies and were analytical except where indicated to the individual preparations. Bis(ethyl vinyl)benzene was supplied by DeGussa Organische Chemie GmbH, Germany.

Pellets of gamma-radioactive General Diesel Company and
uranium oxide from Battelle Metal Company were both used in
the preparations. An uranium-uranium bipartite was incorporated
in the uranium oxide of Battelle Metal Company.

Because of the inherent low uranium grade supplied by
Battelle Metal Company, U.S.A.,

Prismatic hydrosilic of uranium grade 34 pellets from well
analyzing type 212 was used in the calculations where sufficient
concentrations were not maintained.

CHAPTER III

METHODS OF ANALYSIS AND IDENTIFICATION

Silicate determinations reported in this work were carried out by decomposing the sample with sodium manganopropyl silicate according to the method described by Salterey¹³ with subsequent titration of silicate ion by the Volhardt method. Fluorite ion was determined as an aliquot portion of the decomposed solution by the same silicofluoride method described by Miller, Bush and Dickey¹⁴; a modification of the method of Ranta¹⁵ was not chosen and used.

The decomposition used for halogen determination described by Eshel and Turtur¹⁶ involving heating of the sample with nitric acid pretreatment in a sealed tube and separation of fluorite ion by a modification of the distillation procedure given by Eshelby, Welsh and Nease¹⁷ was used to some extent during the first period of this work. However, these procedures, though found to be dependable and accurate, are lengthy and the required apparatus may not readily available at all times.

Refractive indices were determined by means of an Abbe refractometer maintained at constant temperature by immersing water troughs in a refractometer from a constant temperature bath. White light was used as a source of illumination.

A Gay-Lussac type penetrometer modified to include an orifice tube was fitted with a ground glass joint was used to determine densities. The penetrometer was carefully calibrated and had a value of 4.000 ml. Determinations of the density of a given material were made at the same time as determinations of the refractive index and with use of the same concentric suspensions both. This procedure aided in reducing errors in values for index refractions calculated from the Lorentz-Guinier formula.

Values of index refraction from this formula are listed as observed values; calculated values were obtained by addition of the appropriate constants given for the refractivity of the constituents when and whenever necessary to Langmuir.¹²

Densities measured for the boiling points are summarized. Pressures below 50 mm. were measured by a Baratron gauge purchased from the Bellisticle Company. Pressures of 50 to 150 mm. were measured by a Dinesett gauge; pressures exceeding 150 mm. were measured by a single stage bellows gauge.

Relative weight determinations of low boiling compounds were made by the Titter-Supper method.

CHAPTER 27

SUMMARY OF THE LITERATURE

Alkyl ethers containing fluorine and of the general type produced by the addition of alkene to fluorocarbenes^{17,18,19} were obtained by Baugh^{17,18,19}, in 1949 by the action of alkali metal or alkali carbonate on polyfluorocarbonates. This process was adopted and modified by Bedford²⁰ recently in these laboratories. A further study was made of the preparation of fluorethers from saturated compounds.²¹

In 1944 Bedford and Higley² reported the formation of ethers by the addition of alkene to fluorocarbenes in the presence of a basic anhydride. They added ethyl acetate, diethyl phthalate, ethylene glycol, phenol, methanol and cyclohexanol, each to one or one of the following alkynes: tetrabromoethyne, trifluoromethyne, and 1,1,1-trifluoroethyne. Their reactions were carried out in an autoclave under nitrogen pressure and with the alkene produced by the action of metallic sodium on the corresponding alkyned.

In February of 1948 Miller, Fager and Schmitz²² reported the addition of methyl alcohol to tetrafluoromethane, trifluoromethane and 1,1,1-trifluoroethane. They found that these additions presented satisfactorily to glass apparatus at atmospheric pressure.

In the same later work, Hill, Lee and Ladd¹⁹ reported the addition of methyl-, ethyl-, α -methyl-, β -methyl and γ -butyl chlorides to trifluoroacetoacetan. They found that sulphuric acid was necessary for these particular additions and that potassium hydroxide dissolved in the alcohol being used neutralizes any sulphuric acid produced during the reaction.

Hill and Holt²⁰ prepared a number of cyclopolymethylene ethers of the type previously reported by Blasford and Kirby by reaction of the suitable epoxide with the appropriate substituted polyisobutylene. Their method of separation of the various products from distillation from a strongly alkaline solution and they obtained both the substituted epoxide and a polyisobutylene product, the phenylpolymethylene ether, from the reaction of 1,2-dihydro-2,2-difluorocyclohexene and sodium phenoxide. They were able to determine from their more vigorous conditions, the other epoxides being obtained from sodium phenoxide and 1,1,2-trifluoro-1,1-difluorocyclohexene.

CHAPTER V

ANALYSIS OF ALCOHOLS AND PHENOLS BY FLUORIMETRY

A. Fluorimetry.

These reactions, as have been pointed out in the introduction to this work, are here described and are thought to be effected by anisolephiles reagents on the fluorimetric line. If the phenoxide is symmetrically substituted, two only are present in possible, regardless of the various sizes to which the substituent radical may be:

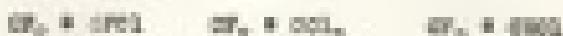


If, however, the fluorimetric is unsymmetrical, two formations of either or both of the possible structurally isomeric ethers may take place, depending on the relative induced or permanent positive charge on the two carbon atoms. For example, in the addition of chlorine to trisubstitutedbenzenes



Formation of 2 fluorine and two carbon bearing one fluorine atom to trifluoromethyl positive, since the addition is by the negatively charged carboxilate anion, while 3D would require the carbon bearing one fluorine and one chlorine to trifluoromethyl positive.

The chlorine atoms for this work were all unsymmetrical and contained the CF₃ group with substitution at one lone pair of fluorine, chlorine and hydrogen on the other carbon as follows:



Arbitrarily, with these chlorine under the conditions studied and with considerations regarding the structure of the adding particulate, addition was in all cases to the carbon bearing one fluorine atom. This could not have been predicted from the evidence of addition of other compounds to unsymmetrical fluorination. In the addition of primary amines, which presumably form resonance, no chlorides which are subsequently hydrolyzed to bisubstituted amines, one or both possible products are formed, depending on reaction conditions.



It was found in the addition of amines, that compound III

was the only oxide prepared at low temperatures, and that both XII and XV were made after the reaction was run at elevated temperatures. Obviously there is ignored in temperature the α factor in selection of the possible reaction mixture.

Nevertheless, a wide variation in temperature of reaction of alkoxide with fluorosiloxane (vide¹) in the addition of alkyl silanol to allyl α -phenyl phenoxyl oxide was observed. Further variations in conditions of the alkoxide synthesis are complicated by the formation of polyalkoxy compounds and also by decomposition of some of the ethers, but even in these cases no products or fragments were identified which could have come from the addition of alkoxide to phenoxyl phenoxyl compound XII.

Addition of alkoxide

The first report of the addition of alkoxide to fluorosiloxane was made in 1946 when Stanford and Whigham² were issued a patent on additions to CH_3SiO_2 and $\text{CH}_3\text{SiOCl}_2$. Some months after the investigation in this laboratory of the addition of alkoxide molecules to fluorosiloxanes was initiated, Miller, Payer and Grimes³ showed that ethanol added to CH_3SiO_2 , $\text{CH}_3\text{SiOCl}_2$, and $\text{CH}_3\text{SiOCl}_3$ to give ethers of the type $\text{CH}_3\text{SiO}_2\text{OR}_2$. After a number of alkoxides had been added to several fluorosiloxanes in this laboratory, Park⁴ and myself published a paper on the preparation of the ethers obtained by adding ethanol, ethanol, α - and β -propiolactone, and methanol to CH_3SiO_2 ,

It was felt that these esters were not of sufficient scope to interfere with the present investigation, the goal of which was to study the effect of various of both aliphatic and fluorine atoms on the rate of addition and the properties of the ethers. Furthermore, it was felt that care should be taken in the proof of structure of the resulting compounds and in the separation and identification of products other than the saturated ethers. The only products reported by previous investigators were the corresponding saturated fluorine compounds.

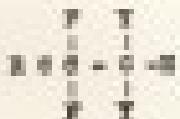
Therefore, the study of the addition of methanol, ethanol, isopropanol and tert-butanol to CF_3COCl , CF_3COOH , and $\text{CF}_3\text{COO}_2\text{Na}$ was made. It is known that the contribution of methyl groups for hydrogen bonding is ethanol; greater an increased contribution of hydrogen bonding is $\text{CH}_3\text{CH}_2\text{OH} < \text{C}_2\text{H}_5\text{OH} < \text{C}_3\text{H}_7\text{OH} < \text{C}_4\text{H}_9\text{OH}$. It was thought that this variation in property might affect both the kinetics of addition as well as the stability of the resulting ethers.

The ethers were chosen because they are the most easily prepared compounds that would illustrate the effect of various kinds of groups on one of the etheric ethers. Also it was felt that ethers made from them would be relatively stable. Tetrafluoroethoxyethane was not included since it has a low boiling point (-40°C) and would give only a single saturated ether. Furthermore, the properties had been investigated previously.

possibly by the de Peau process. The chlorine content would have been interesting to study but no satisfactory methods have been developed for its preparation and, in addition, it was thought that such experiments might result from the use.

The addition of each of the alcohols to the chlorine gave a separated ether as the principal product with the exception of tert-butyl alcohol. The properties of these products are given in Table I. Various experimental conditions were employed in order to obtain the ethers in as high yields as possible since they may conveniently be obtained as discussed below.

Chemical formulas for the separated and the unseparated ethers are shown respectively by I and II below.



I



II

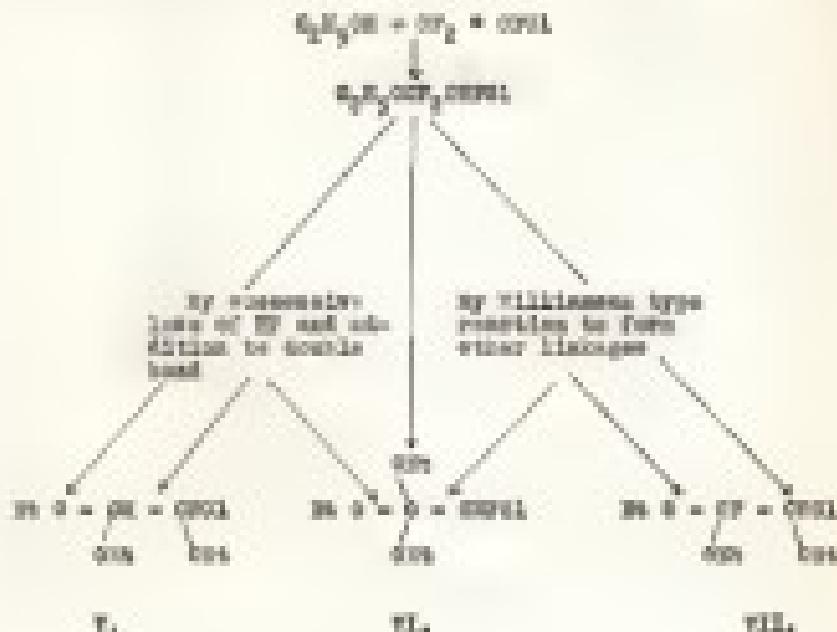
In which F represents an epoxy group and T represents chlorine, chlorite or hypochlorite. The tert-butyl ether may be considered a polyetherchlorite product of an original unseparated ether, though it seems doubtful that the unseparated compound exists for any length of time at the temperatures to which it was necessary to raise the reaction in order to obtain addition.

In a number of cases rather unexpected products were

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found. For example, stable, high boiling compounds were formed by combined reaction of chloro-1,1-difluoro-1,2-dibromoethane, $\text{CF}_3\text{COOC}_2\text{Cl}$, and chloro-1,1,2-trifluoro-1,2-dibromoethane, $\text{CF}_3\text{COOC}_2\text{Br}$ with sodium tripolyphosphate in ethyl alcohol. Helium analysis and calculation of molar refraction indicated that two additional esteroy groups had entered the molecule. For the other three trifluoromethylations and ethyl alcohol, three polyalkoxy structures are possible, depending on the tetrahedral stage of the reaction:



the product obtained was subjected to hydrolysis by concentrated sulfuric acid and ethyl fluorosulfonate was separated from the reaction mixture. Only a product of structure VI, of the orthoester type, could have produced this result. The hydrolysis is in keeping with the susceptibility of these compounds to acid hydrolysis and their relative stability to alkaline media.

There is little evidence for reaction between the two methods of formation of the orthoesters. The two fluorine atoms on a carbon atom with adjacent ether linkage are known to be inertive. Therefore the Willdissene type of reaction was reasonable, although it is not the usual method of making orthoesters except for the orthoesters from chlorofluorocarbons and carbon tetrachloride. Formation through the addition of hydrogen fluoride and addition of alcohol is equally plausible, though the addition of the vinyl ester group to that end of the molecule requires that the polarizing effect of the esterified vinyl group be such that the carbon bearing the ether linkage be made relatively positive. These ether linkages have separated electron pairs on the oxygen atoms, as do the halogen atoms, and are stabilized electron-pairing in resonance structures in because electron-pairing continues although there is electron-shielding. Therefore either



would be expected, or any combination of the two effects, so that the final result leaves the ester with other linkages possibly unscathed.

The olefins $\text{CH}_2=\text{CO}_2$ and $\text{CH}_2=\text{CO}_2\text{Cl}$ were considerably more reactive than the more nearly symmetrical $\text{CH}_2=\text{COCl}$. This would be expected from their markedly enhanced reactivities and was shown particularly by their reaction with propyl alcohol. $\text{CH}_2=\text{CO}_2\text{Cl}$ yielded an addition product at atmospheric pressure and a temperature of $35-40^\circ$ and $\text{CH}_2=\text{CO}_2$ was quite unreactive under similar conditions. The $\text{CH}_2=\text{CO}_2\text{Cl}$ was refluxed for six hours with anhydrous propyl alcohol at atmospheric pressure. 70% of the ester was recovered and an addition product isolated.

Reaction of ethylacetone with $\text{CH}_2=\text{CO}_2\text{Cl}$ and $\text{CH}_2=\text{COCl}$ was possible at atmospheric pressure and at the reflux temperature of the alcohol. This type of ester could be made free of glycerol only at elevated temperatures (120°) the proportion not isolated is no estimate. Of course, this reaction is not necessarily a reaction of the esterified linkage, as has been discussed previously. In reactions involving $\text{CH}_2=\text{CO}_2\text{Cl}$ and $\text{CH}_2=\text{CO}_2\text{Cl}$ with alcohols, the corresponding series of ethyl- and diethylacetone could more frequently be observed, especially when the reaction products were in contact with water

for an extended period. Below are some details of the typical water staining reactions.

In connection with the reactivity of the sulfite, a number of preparations the details of which are presented in the experienced section may be mentioned.

An attempt was made to carry out the addition of phenol to 1,2-dihydro-1,2-dithiin-3-thione, CR₂H₄S₂, by refluxing the sulfide with a solution of phenol and potassium phosphate in acetone for two hours. No addition product was obtained.

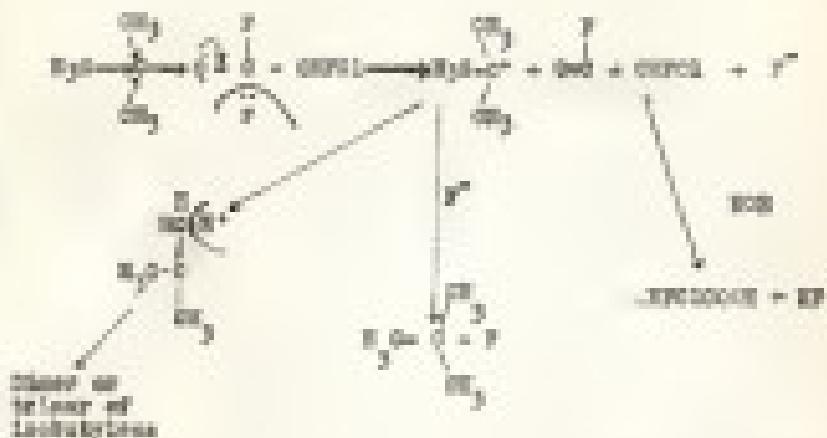
A considerable number of preparations were made by the addition of the various analogs to 1,2-dihydro-1,2-dithiin-3-thione, CR₂H₄S₂, and a product was obtained in each case. However, further investigation revealed that the isolated compound from which the sulfide was prepared, CR₂H₄S₂O₂, contained from 10-25% of the lesser CR₂H₄S₂. The latter compound would produce CR₂H₄S₂ on hydrolysis. Further consideration showed that the physical constants of the products obtained with various CR₂H₄S₂ were practically identical with those of the addition products of chloroacetic acid phenol to CR₂H₄S₂ and that the yields were in the range of 30-50%, which is about the percentage of unreacted 1,2-dihydro-1,2-dithiin-3-thione that could be expected to be present. Hydrolysis of these various products did not reduce but on the contrary increased their yields. This indicates either hydrolysis of the impurities or the spontaneous conversion CR₂H₄S₂O₂.

Stability and decomposition of the alkyl ethers

Ethers formed from addition of straight chain alkyls to aromatic hydrocarbons are relatively stable while those formed from the more reactive 1,1-difluoro-2-hydroxyalkanes and 1,1-difluoro-2-chloroethane have a tendency to split off hydrogen fluoride on long standing.

The stability of fluoroparaffins of the type prepared in this research is influenced greatly by substitution of methyl groups for hydrogen atoms on the alpha carbon of the alkyl group. The isopropyl ether from addition to CPyd₂DCl was obtained only as a mixture of the substituted and unsubstituted compounds, and both tert-butyl ethers from addition to CPyd₂DCl to CPyd₂D₂ were unisolated.

The tert-butyl ethers are particularly interesting in that the esterified form is apparently not stable enough under the conditions of this work to be isolated at all. In an early preparation of the addition product of tert-butyl acetate to xylenebenzene, no ether was isolated but a mixture of decomposition products was obviously Isobutyl Chloride, Fluorotolueneacetic acid and probably a mixture of the two isobutyl esters. These products can be accounted for by neutralization of the following:



Oppositely charged effects would be operative in the isobutyl structure, repelling electrons in the carbon atom linked to oxygen and facilitating removal of the electrons due to loss of the substitutive ion. The scattered electrons on the oxygen would then move towards formation of a double bond, leaving behind, of the fluorine with the pair of electrons. The resulting compound is the alpha-fluoride of fluorobutenone which is hydrolyzed to the free acid. The carboxylic acid formed from the isobutyl residue has the possibility of undergoing a process to become an ester with subsequent polymerization, or of reacting with the fluoride ion to form isobutyl fluoride.

In another experiment isobutyl fluorite and the isobutyl ether were both isolated when the temperature of the reaction mixture was kept below room temperature.

With the vinyl ether and the butyl fluoride we have
assumed for it the following mechanism: the electrons re-
leasing properties of the β,β' -dibutyl group forced the release
of a fluoride ion from the dioxide in the manner indicated
but without rupture of the SF_2 C-F bond. The proton was
then released from the dioxide to give BP and the electrons
from the β,β' -carbons moved to the form a double bond.



The BP thus formed could easily react with excess β,β' -dibutyl
fluoride to form the corresponding fluoride.

This decomposition of the isopropyl ether had been
observed in dimethylsulfide; a pure sample of $\alpha\beta\text{-dihydroxyethyl}$
had successfully decomposed as shown in the experimental section
by heating at atmospheric pressure. Isopropyl fluoride and
dimethylsulfide fluoride were separated and identified. There
was also some indication of the presence of propylene as a
fission product in this stage but since it could not be
purified with sufficient accuracy for the per cent proportion
determination.

The same mechanism as that proposed for the decomposition
of the β,β' -dibutyl ether also seems to be applicable in this
case.

ANALYSIS OF PHENOLS.

It has been shown previously that phenols will reduce the double bonds of unsaturated fluorocarbons to give a single product in which the vinylic group is reduced to the carbon thus holding the greater number of methyl groups. However, again, as noted above, under the proper conditions will add to either end of the vinylic hydrocarbon double bond, is most active, and will therefore give a mixture of products. It was also thought that phenols might add to unsaturated fluorocarbons to give stereoisomeric products, since the phenoxide ion is less basic than the alkoxide ion.

Aryl Fluorocarbonates have been prepared before. Thus 1 mol. Phenol added to tetrafluorobutene under anhydrous conditions is an epoxide⁹ and others are easily¹⁰ prepared via epoxides by the reaction of sodium phenoxide with unsaturated fluorocarbon epoxides. In table III is a comparison of the properties of two of the ethers they prepared from the above-mentioned fluorocarbon epoxides with those obtained by the addition of phenol to the two starting materials since those saturated ethers are dihydroisologated. In the case of each pair of preparations it can be seen that there is a good agreement in the boiling points, freezing points and refractive indices of the ether. Except, in one case where the two epoxides are prepared together the saturated ethers or the corresponding vinylidene epoxides are used in the starting materials.

TABLE II

Reaction	$R_1 R_2 C_6 H_4 Cl_2$	$R_1 R_2 C_6 H_4 Cl_2$	η_{sp}^2
$C_6 H_5 CH_2 + Cl_2 C_6 H_4 Cl_2 \longrightarrow C_6 H_5 Cl C_6 H_4 Cl_2$	48	abs	1.4119(16)
$C_6 H_5 OH + Cl_2 C_6 H_4 Cl_2 \longrightarrow C_6 H_5 Cl C_6 H_4 Cl_2$	72	abs	1.4119(16)
$C_6 H_5 CH_2 + Cl_2 C_6 H_4 ClO_2 \longrightarrow C_6 H_5 Cl C_6 H_4 ClO_2$	56	-51	1.4117(16)
$C_6 H_5 OH + Cl_2 C_6 H_4 ClO_2 \longrightarrow C_6 H_5 Cl C_6 H_4 ClO_2$	57	-51	1.4118(16)

In the reactions involving the substituted aromatic hydrocarbons it appears that the chlorine of the α -C₆H₄ group has been replaced by the phenyl group in a Villanueva type of reaction. This is consistent enough and better and well with the statements concerning the "General concept of the reactivity of the organic chloroformate indicates that the chlorine atom or carbon atom bearing no fluorine atom would be replaceable." However, this group apparently reacts without and, in fact, seems to have no activating effect on the adjacent fluorinated grouping.²

There is, as we know, that possibility will add to a number of possibilities if some resonance is among them the replacement of a fluorine by the chlorine atom of the α -C₆H₄ group will not appear as a single displacement reaction. It is not necessary to assume such a reaction if we consider that in a basic reaction the hydrogen which migrates to the α -C₆H₄ group may be removed as a proton induced by the loss of a chloride

less to four hydrogen atoms, such an substitution reaction would result in the formation of an ester and this derivative was observed by these investigators.

In order to indicate more fully the probable reaction mechanism, a study was undertaken of the reaction of phenol with CH_3COCl and $\text{CH}_3\text{CO}_2\text{H}$. If the Williamson type reaction occurs with the first compound, then $\text{CH}_3\text{CO}_2\text{OCH}_2\text{Cl}$ should result. However, if the reaction proceeds via esterification, then the acetate ether, $\text{CH}_3\text{CO}_2\text{OCH}_2\text{OCH}_3$, should result from both substituted fluoranthene. Considerable difficulty was encountered in separating and identifying the products. It should be pointed out that certain ethers are less stable than others; for example, in the alkyl ethers, as noted, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5/\text{H}_2\text{O}$ is considerably less stable than $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5/\text{H}_2\text{O}$ apparently the more highly substituted the β -carbon the more stable the $\gamma,\alpha\text{-dIL}$ isomer.

It is reasonable to assume that an ether such as $\text{CH}_3\text{OC}_2\text{H}_5$ might decompose to give a variety of products; if such is the case, it would explain the fact that an unisolated fluoranthene was identified.

It is difficult to establish the structure of a phenyl fluoranthene by the method used with vinyl fluoranthene saturated vapors and not enough of the α -phenylvinyl phenyl ether was synthesized to establish its structure conclusively. However, data obtained from a series of experiments with ethanolic solutions that CH_3COCl reacts to give $\text{CH}_3\text{CO}_2\text{OCH}_2\text{Cl}$ when

ethyl acetate was formed during the reaction¹².

While these experiments do not conclusively prove that esterification is required before addition with aqueous methanol the α -C₂H₅ group, they at least give this indication.

In connection with the addition or removal of the phenyl ester, it is interesting to note that states and fails obtained the same product when sodium phenoxide was reacted with C₂H₅COOC₂H₅ as with C₂H₅COONa. In other words, the following reactions took place:



This either is the same obtained in the present work from the addition of phenol to C₂H₅COOC₂H₅. The possibility of esterification in reaction (a) has been discussed above. In Hahn and Schulte report, however, no satisfactory explanation is given for the formation of the same end product by reaction (b). In this case, formation of the ester by dehydrochlorination is not possible since the chloroform is completely unreacted. There is, however, another possibility of esterification that should be given consideration. There are a number of experiments recorded in the literature in which treatment of α , β -diketones suspended with alkali metals hydronium resulting in removal of the two acidic atoms but not in the expected manner as the hydroxide sodium.

For example, Szwarc²⁴ treated the kinetics of 3,4-dihydro-2H-pyridine with alkyltin pyridinium hydrosulfide and obtained no sulfide containing no halogen:



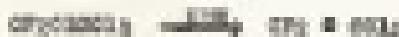
Other examples are given by Park²⁵,



and by others²⁶



Each of these cases is a source of halogen from a carbon attached to a strongly electron-attracting group. The halogens, particularly the fluorine atom, attached to the carbons of the heterocycles used by Miller and Bell may have a similar influence since they are highly electronegative. Therefore no sulfide may be formed.



It has been shown in this work that addition of phenol to this sulfide will prevent the ether reported by Miller and Bell.²⁷

The effect of the addition temperature on the yield of the ether is quite significant. In experiments with tri-

Fluorotetrahydrofuran and phenol, the best yields were obtained at 40°, although at lower temperatures gave lower yields and at 60° no ether was formed. Best yield yields were obtained with the amounts by varying only the addition of the various temperatures of various which was used as the solvent.

The addition to CH_2NO_2 was carried out both at 30° where the corresponding ether was obtained in + 95% yield. In this case higher addition temperatures resulted in the formation of fluorotetrahydrofuran phenol ether. Separation of the product from the starting material by still distillation also resulted in dehydrofluorination. Since it was difficult to remove the unseparated ethers from the desired products, one had to be content to prevent their formation. The ether from CH_2NO_2 also dehydrofluorinated rather easily, on the other hand the esterols prepared from trifluoroethoxybenzene were resistant to alkali. For example, the phenyl ether was refluxed with 50 potassium hydroxide at 110° for 24 hours without any appreciable change.

In Table III are listed some of the properties of several ethers prepared by the addition of phenols to various esters.

Another should also be made of the fact that these and perhaps most of structures are based mainly on the assumption that a structure with the two fluorine atoms on the carbon bearing the ether linkage would entitle the fluorine sufficiently to react with nucleophilic potassium hydroxide. Thus the ether prepared reacted with the alkali to give a phenol.

containing no fluorine, they concluded that their proposed structure was correct.

A much simpler and straight forward proof of structure by hydrolysis of the ester was reported on as illustrated below for the acetate product of phenyl 4-hydroxyisobutyrate.



Several attempts were made to hydrolyze this ester to a product that would establish the structure of the original ester before the procedure described below was worked out. However, from the original ester $\text{C}_8\text{H}_{11}\text{O}_2\text{COOC}_2\text{H}_5$, hydrolysis with sulfuric acid by the method of Tracy and Sherman¹⁴ would give the phenyl ester of phenylisobutyric acid. However, this ester is apparently more easily hydrolyzed than the acetyl ester of the isobutyrate acid and it could not be isolated by the normal ester ether. Isolation of diisopropenylsulfide was not practical, since this material is difficult to handle and could not be distilled easily from the excess concentrated sulfuric acid required for hydrolysis without decomposition.

The method finally adopted for proof of structure of the phenoxy-isobutyrylphenoxide involved the formation and isolation

of the ethyl ester of the isobenzoic acid without separation at the cold stage from the products of hydrolysis. Since by this procedure, ethyl 2-methoxybenzoate was isolated, the original ester must have had the structure $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$, and thus the reaction proceeds with phenolic in a manner similar to that with alcohols.

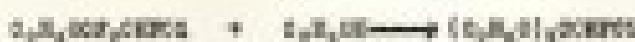
II. EXPERIMENTAL

ADDITION OF ALCOHOLS

In general, reaction of the fluorocarbon with the various alcohols was carried out to give optimum at atmospheric pressure. In the case of tert-butyl alcohol, however, the use of an addition with the reactants under an oxygenless pressure was necessary. The temperature of the reaction was determined, as is the reaction of fluorocarbon with paraffins previously described, by the solubility of the alcohol, miscibility of the product in carbon tetrachloride and also by the degree of miscibility of the particular alcohol. A brief outline of the procedure for these reactions cannot be given (a given below; specific details will be found under the descriptions of the individual reactions).

The alcohol was placed in a three neck glass flask equipped with stirrers, reflux condenser with dry ice cooled top situated in the upper and not direct tube or direct addition funnel. Solid potassium hydroxide (90% KOH) was added and dissolved. The alcohol was added into the alkali with stirring. Mixing of the reaction mixture with water causes the weak ester to separate and this product was washed with water until free of alkali and reasonably free of alcohol, then dried and fractionated.

ADDITION OF tert-BUTYL ALCOHOL TO PROPENE, $\text{CH}_3 = \text{CH}_2 + \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$



a. One hundred eighty three grams (1.5 moles) of potassium hydroxide was dissolved in 450 ml. (approx. 0.5 moles) of ethyl alcohol in a three neck flask equipped with stirrer, reflux condenser cooled with dry-ice and liquid nitrogen projecting under the surface of the liquid. Tetrahydrofuran (150 grams) (1.0 mole) was distilled into the stirred mixture over a period of three hours, unreacted alcohol being returned to the reflux condenser. Separation of the reaction mass to 45°. The reaction mixture was allowed to stand for two hours, then heated to a liquid temperature of 75° for 1 hour at this point there was no reaction of ester. The crude product was separated by diluting the reaction mixture with water, washed with water and dried over anhydrous calcium carbonate. Dissolution through a small column packed with glass helices gave 110 grams of poly(ethoxyethoxy), $\eta_{D^2} = 0.14 - 0.15$.

Further dealkylation by halogen analysis, etc., or this ester are not made since this compound had been previously reported and its structure determined. A number of preparations of this ester have been made with yields to a maximum of 93% of theoretical. The ester as prepared above was used in the preparation of the triethoxy compound described in (b).

b. Fifty five grams (0.45 mole) of poly(ethoxyethoxy), 110 grams (1.7 moles) potassium hydroxide and 100 ml. (approx. 0.5 moles)

methyl alcohol were placed in the extraction vessel, extracted and heated with heating for 3 hours at 120°. The extraction was cooled to room temperature before opening. This pressure was released and nonflammable gas emerged from the reaction mixture was diluted with water. The aqueous layer was separated, washed with ether and dried over anhydrous calcium chloride. Fractionation gave only one product, 10 grams of 1,1,1-triethyl-2-fluoro-3-chloro-1-propanone, b.p. 41-42 m. 47.5°, δ_1^{25} , 1.4830, δ_2^{25} 1.9113, 100. (m.s.) 26.36 (obs.) 26.35, 102. (m.s.) 48.28 (obs.) 48.2.

The esterester, 1,1,1-triethyl-2-fluoro-3-chloro-1-propanone was subjected to acid hydrolysis to determine its structure by the following procedure: 10 ml. of sulfuric acid (96%) was added slowly to 10 grams (9.08 mols) of the esterester with tetrahydrothiophene stirring. After 3 ml. of the sulfuric acid was added, there was no additional separation of react., an additional 3 ml. of sulfuric acid was added, the mixture allowed to stand 30 minutes, then poured into cold water and the aqueous layer separated. This product was washed two times with cold water and dried over anhydrous calcium chloride. Fractionation gave 4 grams of methyl fluorochloroformate, δ_1^{25} 1.3000, b.p. 125-130°, δ_2^{25} 1.9113, indicating that all three ethoxy groups were on one carbon and that the compound was the esterester of fluorochloroformic acid.

Addition of pentylene sulfide



Pentene diethyl-sulfide was prepared by refluxing pentyl alcohol with excess sodium until the solution was saturated with the anionate at approx. 180°; 270 ml. of this anionate were dissolved while hot into the anionate ether solution, the temperature of the mixture lowered by cooling in a Dry-ice bath and 50 grams (4.5 mols) of trifluoroethanesulfonates added. The mixture was heated with stirring for 30 hours at 100°, then cooled to an ice-salt bath to approximately -40° and the contents transferred while cold to the top of the fractionating apparatus. The contents of the apparatus were held to 100°. To avoid decomposition, the product was not heated above 35°. At this temperature and at atmospheric pressure, the product was distilled and identified as diethyl fluoride, bp. 13.5°, nD₂₀ 1.396 (value) 14 (1934) 13.

Treatment of the fractionating system containing the residue from the above distillation was lowered gradually to approx. 45° and the pot maintained at 35° and the head of the condenser cooled liquid air at -40°. The product was distilled until the pressure reached 30 mm. At this point the cooled distillate and nine previous preparations had shown that the ether and aldehyde were not separated by distillation, the remaining material was removed from the pot, cooled three

times with cold water and dried in the refrigerator over anhydrous calcium chloride. Fractionation gave 10 grams of 1,1-bis(2-methylpropoxy)-1,3-difluoro-2-oxopropane, (III), m.p. 10.0° m. $\lambda_{\text{D}}^{25} 207^{\circ}$, ± 7.0 m. $\lambda_{\text{D}}^{25} 107^{\circ}$, $d_4^{25} 1.3717$, $d_4^{20} 1.374$, f.p. -20°, 202 (m.p.) 10.0 (m.p.) 10.0, σ^2 (m.p.) 20.29 (liter) 21.6.

Addition reactions of tert-butyl iodide to (II) at 0°C. under other conditions are described in some detail below since the positive products were of interest although the other described were not separated as the final products.

a. Fifty-eight grams (0.1 mole) of trifluoromethanesulfonic acid (III) and 140 ml. of tert-butyl iodide were heated with sodium tert-butylate until the esterified salt成立了 for 10 hours at 100°. The reaction mixture was diluted with cold water, the crude product separated, washed and dried and fractionated in atmospheric pressure to give out 1.6 grams, b.p. 45.0-45.5°, identified as tert-butyl fluorite, a mixture of isomeric diesters fractions, and 1.5 grams of diisobutylketone m.p. 40.0-40.5°, $d_4^{25} 1.4473$, $d_4^{20} 1.4514$, 201 (liter) 11.62 (liter) 10.4, reported constants reported¹² for this acid are b.p. 38°, $d_4^{25} 1.4459$, $d_4^{20} 1.4537$.

b. Fifty-eight grams of trifluoromethanesulfonic acid (III) and tert-butyl iodide were passed in the esterified and heated with sodium tert-butylate until 10 hours at 100°. The esterified salt成立了 in a Dewar flask bath, separated and concentrated atmospheric pressure, a loss compensating the original material with added tert-butyl iodide.

above was heated to 100° and 41% material distilled at this temperature removed. Distillation of this distillate at 100° was stopped to the maximum, therefore the mixture was diluted with ether, the organic layer separated and dried. This product decomposed on heating and separated into two distinct layers, the upper one colorless.

The residue remaining in the solution after the first distillation was extracted with ethyl ether, the ether removed from the extract by distillation and the residue fractionated under reduced pressure to give 40 grams of $(CH_3)_2COH$ at $0^{\circ}C$, b.p. ± 100 mm. $n_{D}^{20} = 16.3^{\circ}$, $n_D^{20} = 1.3674$, $d_4^{20} = 1.063$, 100% (caust.) H_2O (Anal. Calcd.). This material was probably pure and it began to decompose rapidly, forming two distinct layers as noted above. Distillation of these decomposition products gave two fractions: frac 1, b.p. to 110° and frac 4, b.p. 110° , $n_D^{20} = 1.4075$, probably fluorescein-sodium salt. frac 1 continued to decompose, separating again into two layers. A portion of the lower layer was removed and distilled to 100° . The distillate had a refractive index of 1.4038 at 40° , a density less than 1.0, checked bromine, reacted very slowly with sodium and gave only a trace of hydrogen on sodium fusion. Consideration of the source and these findings indicates that this material was a mixture of stored tri-n-octylamine.

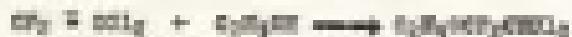
b. Reaction of 0.5 mole of triphenylbenzene with 250 ml. of $100:1$ -ethyl alcohol or with propoxyethyl alcohol and 0.5 mole of sodium in the solution for 10 hours at 100° gave

size of the tetraglycidylesters, dilution of the reaction mixture with water (one g) gives of water insoluble material which, on distillation, yields 27 grams of material, b.p. 94.3-95.5°, n_D^{25} 1.4916, n_D^{25} 1.4919 and a residue of 26 grams of viscous, silver-white colored material that could not be distilled even after the pressure in the system had been lowered to 2 mm.

In these experiments it seems probable that the lower-boiling material prepared was the epoxide diene reported by Baumann ¹⁴ as having the following properties:

Structure:	$\text{CH}_2=\text{CH}-$
	$\text{CH}_2=\text{CH}-$
b.p.	94.5°
n_D^{25}	1.4916
n_D^{25}	1.4919
n_D^{25}	1.4919

The viscous material is believed to be a higher polymer of the dieneopholeic or possibly a copolymer of linoleic acid and linolenic acid. No further identification of these products was attempted.



Forty six grams (0.05 mole) of potassium hydroxide was dissolved in 300 ml. (approx. 3.5 moles) of acetyl acetate (99%) and 77 grams (0.10 mole) of 1,1-bis(2-methoxy-2,3-dihydrophenyl)-ethane distilled over a period of 3 hours into the potassium acetate solution contained in¹⁴Tubes with flasks equipped with condenser and reflux condenser cooled by water at about 3-4°. The reaction temperature rose rapidly to 70°, but was lowered to 40° by external cooling and maintained at this temperature. There was no efflux of diethyl during the course of the reaction. After addition was complete, the reaction mixture was cooled to room temperature and diluted with water; the lower layer was separated, washed with water and dried over anhydrous potassium carbonate. Fractionation through a 20 inch column packed with Kieselguhr gave 37 grams of ethyl-1,1-bis(2-methoxy-2,3-dihydrophenyl)-ethane, C₂₂H₂₆O₂, 49% (theory). Subsequent preparations averaged 49%. b.p. + 100 mm. 63-65°, n_D²⁰ 1.5352, d₄²⁰ 1.1049, 1% Et. (calcd.) 37.7 (obs.) 39.0, and 4.5 grams of 1,1,1-triethyl-2,3-dihydrophenane, (triethyl-phenoxy), b.p. + 65 mm. 37-38°, n_D²⁰ 1.4734, d₄²⁰ 1.1354, 91% (calcd.) 90.0 (obs.) 90.0, 100% (calcd.) 99.0 (obs.) 99.0.

The esterether, triethyl-1,1-bis(2,3-dihydrophenyl)-ethane, was prepared in larger quantity by reacting 50 grams (0.05 mole) of the ether, triethyl-1,1-bis(2,3-dihydrophenyl)-ethane, with 1.5 moles of anhydrous sodium acetate in 300 ml. of absolute acetyl acetate. The mixture was refluxed for 4 hours, cooled and diluted with cold water. A thick emulsion was formed and the product was extracted from this

reaction with vinyl chloride. The ether solution was dried over anhydrous calcium chloride, the ether removed by distillation at atmospheric pressure and the crude esterether fractionated at reduced pressure in a small column packed with glass helices. 115.5 grams of 1,1-bis(2-chloroethyl)-2-chloroethane, b.p. = 60 mm. 104.0-105.0°, was obtained.

This material was as described briefly below, this reaction produced none of the ether or esterether described above as a direct product but vinyl chloroacetate was obtained in 20% yield along with the ester ether. 197 grams (1.0 mole) of potassium hydrosulfide, 51.5 ml. (6.0 moles) of ethyl alcohol (99%) and 120 grams (0.81 mole) of vinyl chloride were refluxed (liquid temperature 90°) for 4 hours, the mixture diluted with water and the organic layer separated, washed and dried over anhydrous calcium chloride. Fractionation gave 35 grams of vinyl dichloroacetate, b.p. = 40 mm. 102.5-103.0°, ν_{max}^{25} 1,4151, δ_{max}^{25} 1,3919, 121 (weak), 49.2 (shar.) 49.5, 102 (shar.), 30.5 (sharp) 30.2.

Addition of Isopropyl Alcohol



110 grams (0.61 mole) of sodium was reacted with 400 ml. of isopropyl alcohol, the mixture cooled to 10° in a three neck flask equipped with stirrer and hot cooled reflux condenser and 120 grams (1.1 mole) of 1,1-bis(2-chloroethyl)-2-chloroethane added dropwise. Temperature of the reaction was

distilled at 20-25° by reduced boiling and collected under oil for three hours. The reaction mixture was poured on to crushed ice, the organic layer separated, washed with cold water, and dried over anhydrous calcium chloride in the refrigeratory. Then this product was placed in the distillation apparatus and the pot heated to 50° with the head reflux maintained at -40° more or less reflux. Therefore the pressure was lowered in small steps to a station of 7 mm. and the product decomposed at this pressure to give 1.5 gms. of (dimethylaminopropylidene)bisbenzene, (80% of theoretical), bp. = 7 mm. 20-25°, n_D^{25} 1.4977, d_4^{25} 1.0311, (calcd.) 26.73 (found) 26.43.

Addition of Dimethyl Alcohol



Twenty grams (0.08 mole) of 1,1-dimethylbenzene and 22.5 ml. of a solution of sodium lignophenolate in butyl-tert-butyl alcohol (adjusted at 100°) were placed in the distillation apparatus and heated with stirring at 100° for 10 hours. The extraction was then cooled to an interval with, opened, and the contents poured into a distillation pot surrounded by an ice bath. Distillation of this material to a maximum pot temperature of 40° at atmospheric pressure gave one product, b.p., 9.0-10.0°, presumably lignophenyl fluoride as had been anticipated before in the addition of this alcohol,

to trifluoromethane.

The residue from the distillation was recovered, diluted with cold water and the organic layer separated washed and dried. Fractionation gave 34.9 grams of (2,3-difluoro-1,1-dimethylpropyl)acetyl- β -diketone, (CH₃)₂C(CH₂)COCH₂COCH₃, b.p. = 41.9 m., 21.8°, n_D²⁵ 1.4334, d₄²⁵ 1.1468, 200 (cacl.) 37.9 (meas.) 37.8.

ADDITION OF 1,1-DIFLUORO-1-ALKYL ETHERS

Addition of methyl alcohol



Thirty grams (1.0 mole) of acetyl chloride was dissolved in 300 ml. (5.0 moles) of methyl alcohol contained in a three neck flask equipped with stirrer and reflux condenser; 137 grams (1.05 moles) of 1,1-difluoro-1-ethoxyethane was added slowly over the stirrer refluxed, (liquid temperature 21°) for 4 hours. The reaction mixture was diluted with cold water the organic layer separated, washed and dried. Fractionation gave 60 grams of acetyl-1,1-difluoro-1-ethoxyethane, (77% of theoretical) b.p. = 130 m., 21.9-22.0°, n_D²⁵ 1.3368, d₄²⁵ 1.2332, 200 (cacl.) 87.0 (meas.) 87.0.

Addition of isopropyl alcohol



Fifty-six grams (0.8 mole) of potassium hydrosulfide was added to 834 ml. (3.2 moles) of isopropyl alcohol and stirred until dissolved. 107 grams (1.33 moles) of 1,1-difluoro-2-chloroethane was added over a period of 8 hours and the temperature of the reaction rose to the reflux point of isopropyl alcohol. The reaction mixture was quenched with cold water, washed, and dried over anhydrous calcium chloride in the refrigerators. Fractionation of this material gave a product of b.p. + 121 mm. $\delta_{\text{D}}^{25} 0.97$, $\delta_{\text{D}}^{25} 1.313$, $\delta_{\text{D}}^{25} 1.37$. Dissolution of the higher fraction and the fact that some decomposition had taken place to produce traces of hydrogen fluoride indicated that this product was a mixture of the unreacted ester and a dehydrofluorination product or vinyl ether.

Fifty grams of the product described above was treated with 13 grams of boron to convert the vinyl ether to a higher boiling product. Since boron has destroyed by action trifluoro-, the product washed with water and dried. Fractionation gave 14 grams of 1,1-difluoro-2,2-difluoroethane, b.p. + 121 mm. $\delta_{\text{D}}^{25} 0.97$, $\delta_{\text{D}}^{25} 1.373$, $\delta_{\text{D}}^{25} 1.387$, 901 (min.), 122.4 (abs.) 121.1.

ANALYTICAL DETERMINATION OF ALKYL FLUOROCARBONS.

The decomposition of the alkylpolyfluorocarbons had been observed in a number of publications, particularly those dealing with esters containing only two fluorine atoms, e. g., propyl

of the other resulting from addition of isopropyl alcohol to 1,1-difluoro-2-chloroethane, was quantitatively decomposed under controlled conditions by the following procedure: 10 grams (0.05 mole) of 1,1-difluoro-2-chloroethyl, 1,1-difluoro-2-chloroethane, ($\text{CF}_3\text{CH}_2\text{CH}_2\text{Cl}$), was dissolved in a glass flask under a condenser cooled by water at $3-4^\circ$. Vapor passing through the rubber container was led through a 120 cc. tube containing a bed of active alumina to absorb hydrogen fluoride and was passed to a trap cooled by a dry-ice acetone bath.

Dissolution of the distilled material gave the entire 1 gram of b.p. $40-5$ to $45-6^\circ$, probably a mixture of propene and isopropyl fluoride and 19 grams of isopropyl fluoride, b.p. $45-6$ to $47-8^\circ$, b.p. 49.4. Dens. 0.71 (obs.) 0.71.

Dissolution of the residue in the flask after the decomposition described above gave 16 grams of dichloromethyl fluoride, 180 kg/cm², b.p. 45-5⁰, n_{D}^{20} 1.3946. Reported boiling point and refractive index of this compound are 49.5⁰, n_{D}^{20} 1.3942. Dichloromethyl fluoride was made by reaction of the product with acetone and had a n.p. 119-120⁰ (b.p. 127⁰).

A small amount of higher boiling material was not distilled. This was presumably, dichloroacetic acid, which gives no discernible boiling point at atmospheric pressure.

4. EXPERIMENTALANALYSIS OF PRODUCTS

All reactions of the fluoresceins with phenol and the steroids were carried out in glass apparatus, specifically, a three neck flask equipped with reflux condenser, stirrer and suitable inlet apparatus for introduction of the reagents. The reactivities of the steroids are determined by consideration of the reactivity of the steroid and also by the susceptibility of the product to hydrolysis¹. In general, the method of preparation of each product was as follows: the fluorescein compound was dissolved in acetone, solid potassium cyanate (KOCN) was added to precipitate the phenolates and the steroids introduced so the mixture was stirred. After completion of the addition of the steroids, the reaction mixture was allowed to stand several hours, then diluted with water and the crude product separated. This product was washed with either aqueous ammonia to convert unreacted phenol to the sodium salt, washed free of alkali, dried and fractionated through a suitable column.

ADDITION TO 1,4-BENZODIHYDROPHENANTHRENEAddition of phenol

The isolated slightly green (2 mols) of phenol was dissolved in 300 ml. of acetone, 36 gms (0.73 mols) zinc pyridine hydrazide added and the mixture stirred until oxidation was complete. The zinc hydrazide was, 116 gms (0.72 mols) was distilled into the acetone mixture through an U-tube passing under the surface of the liquid over a packet of zinc borate at a liquid temperature of 40°. The zinc dust residue was washed by a dry-ice acetone mixture and a trap coated by dry-ice acetone to remove unreacted zinc. After evaporation of the acetone the residue, the acetone was allowed to stand several hours at room temperature, diluted with water, washed with excess sodium hydroxide solution and dried over calcium pyridine carbonate. About 210 ml. of urea product was obtained. Very little carbon was noted passing the reaction and no unreacted zinc was collected in the trap. The product was fractionated through a column packed with glass helices and gave 76 gms of Phenoxyl-1,3,5-tris-fluoromethoxybenzene, $\text{C}_8\text{H}_7\text{O}_2\text{F}_3\text{C}_6\text{H}_3$, b.p. 141.4° at 4 mm, n_{D}^{20} 1.4434, d_{4}^{20} 1.3394, 301 (molar) 16,34 (cm.²) 14,73, $\log \epsilon$ 4.13.

Addition of urea.



The isolated slightly green (2.1 mols) of urea was dissolved in 300 ml. of acetone and 36 gms (0.73 mols)

solid potassium hydroxide added with stirring and external cooling of the solution. One hundred forty seven grams (1.07 moles) of trimesic anhydride was distilled into the stirred solution of sodium and sodium acetate, maintained at a liquid temperature of 23-40°, over a period of two hours. Distilled water was dropped and measured until consumed. The reaction mixture was then diluted with water, the aqueous layer separated and washed with a solution containing 1.0 mole of sodium hydroxide and the product dried over anhydrous calcium chloride. Yield of crude, dry product was 134 grams, 70% of theoretical. Fractionation of this product through a 30 inch column packed with basic alumina gave 106 grams of trimesic anhydride, m.p. 180-181.5°, d_{4}^{20} 1.4917, d_{4}^{25} 1.4933, 106 (calcd.) 13.73 (found) 13.77.

ANALYSIS OF PRODUCT.



The neutral aqueous phase (1.0 mole) of acetone was dissolved in 350 ml. of acetone, 56 grams (0.05 mole) of solid potassium hydroxide added and the mixture stirred until the potassium hydroxide had dissolved. 100 grams (0.05 mole) of trimesic anhydride was suspended and suspended through the solution, maintaining a liquid temperature of 23-40°. The mixture was allowed to stand overnight, then filtered with

1.0 liters of water and 1.0 liter of carbon tetrachloride added. The acidic portion was separated, washed free of alkali and dried over anhydrous calcium chloride. The oil of the acidic, fatty product was 214 grams, 95% of theoretical. Fractionation of this material through a 30 inch column packed with Celite columns gave 167 grams of β -methyl-phenoxy-1,2-dichloroethane, δ_{D}^{25} 1.0702, n_{D}^{25} 1.5494, IR (ester) 13.37 (cm.) 13.41.

ADDITION OF POTASSIUM



The required sixteen grams of (0.8 moles) potassium were dissolved in 350 ml. of acetone, 48 grams of potassium hydroxide added and the mixture stirred until all solid was dissolved. One hundred twenty nine grams of dichloroethane was heated through the solution over a period of six hours, including a liquid temperature of 50° by external heating. The acidic product was separated by dilution of the reaction mixture with water. An additional potassium hydroxide was added to the basic solution. The product, dried over anhydrous calcium chloride, fractionation gave 167 grams of β -methyl-phenoxy-1,2-dichloroethane, δ_{D}^{25} 1.0702, n_{D}^{25} 1.5494, IR (ester) 13.37 (cm.) 13.41.

ADDITION TO 1,1-BIS(2-METHOXY-2,2-DIMETHYLPROPYL)addition of Phenol.

The heated forty-nine grams (2.0 moles) of phenol was dissolved in 350 ml. of acetone, 47 grams (1.0 mole) potassium hydroxide added and the mixture stirred until all solid had dissolved. The solution was then cooled to 20° and 134 grams (1.18 moles) of 4-nitroacetanilide dissolved into the solution while stirring over a period of two hours. Preparation of the reaction mixture was continued at 20° by continuous stirring. The mixture was allowed to stand overnight, then diluted with 2.5 liters of cold water containing 1.5 moles of sodium hydroxide in solution. The crude product was separated, washed free of excess salt with cold water and dried over anhydrous calcium chloride. Fractionation gave 137 grams (64% of theoretical) of phenoxyl-1,1-bis(2-methoxy-2,2-dimethylpropyl), $\text{C}_6\text{H}_5\text{OC}_6\text{H}_2\text{CH}_2\text{CH}_2\text{C}_2\text{H}_5$, $n_{D}^{20} = 1.6165$, $d_{4}^{20} = 1.1775$, 192 (m.p.) 20.0 (m.p.), 21.0.

ADDITION TO 1,1-BIS(2-METHOXY-2,2-DIMETHYLPROPYL)addition of Phenol.

The heated forty-five grams of (2.5 moles) of phenol,

was dissolved in 450 ml. of acetone, 100 grams (1.9 moles) of potassium hydroxide added and the mixture stirred until all solid had dissolved. The reaction was cooled to room temperature and 113 grams (1.19 moles) of dibutyltin oxide dissolved in acetone was added to the mixture. The mixture was stirred until the reaction was complete and the solution was filtered into the acetone. Separated solids were washed and recrystallized, three passes being required for complete separation of the solids. Approximately three hours was required for separation of the solids and the temperature was raised to a maximum of 45° . The reaction mixture was stirred an additional of three hours, allowed to stand overnight, the filtrate with water and the crude product separated. This product was washed with acetone hydroxide solution, with water and dried over calcium sulfate etherite. Fractionation through + packed column + 4 ml. gives:

Distillate	Time	$\frac{D}{D_0}$
I	32.0-34.0	10 hr. 1.4770
II	34.0-35.0	10 hr.
III	35.0-37.0	10 hr. 1.4730

Distillate I is $D_0 = 0.9707$, $D_{10} = 1.4770$, $D_{30} = 1.4730$, $D_{35} = 1.4730$, $D_{37} = 1.4730$, $D_{38} = 1.4730$, $D_{39} = 1.4730$. This product was prepared by Baker and Held. The more accurate are the bromine values reported with their values. Distillates II and III are mixtures of the separated ethers described above and the de-oxydibutyltin product $D_0 = 0.9707$. 40 grams of Distillate I was refluxed with excess potassium hydroxide solution for 4 hours, separated, washed and dried. Fractionation at room

dried pressure gave a product with refractive index of 1.4934 at 25° and containing 27.7% esterine. Reported values for the phenyl-vinyl ether is at 25° 1.4945 and the theoretical value for percentage esterine is 26.5%. Therefore the product obtained by the alkali treatment is probably also a mixture of the methylated and unmodified ethers, but containing more of the unmodified than the L ether.

DETERMINATION OF POLYMERIZATIONS

Pure-diluted-Etherations



Addition of phenol to 1,3-difluoro-2,2-dibromopropane at a higher temperature and with separation of the product by a procedure different from that described above for the unmodified ether resulted in a dehydrohalogenated product.

One hundred eighty two grams (1.0 mole) of phenol was dissolved in 300 ml. of acetone, 45 grams (0.44 mole) of potassium hydroxide was added and the volatile esterine which still could stand was removed. Then, difluorobromopropane (250 grams/2.3 mole) was titrated slowly into the stirred acetone over a period of three hours. A raised temperature flame was used during the addition of the esterine. After addition of the esterine was complete, acetone was distilled from the mixture to a distillation temperature of 75°, the residue weighed

and sufficient potassium hydroxide added to convert the phenol to the potassium salt. The mixture was then dried, distilled, separated, washed with water and dried. Distillation through a 15 foot column packed with glass helices gave 109 grams of phenyl-*o*-phenylene-*o*-biscinnamate, $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$, (23), or theoretical 94.9 g., $T_{\text{d}}\text{,D} = 27.5^{\circ}$, η_0^{25} 1.0192, d_4^{25} 1.13444, 90% (theoretical) 24.2%.

Isomerization of Phenylcinnamate



The esterified ether $\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{CO}_2\text{Na}$ resists isomerization under the previously given conditions of preparation or the conditions of ether distillation in the presence of alkali.

Twenty three grams of $\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{CO}_2\text{Na}$ was refluxed with 20 grams of potassium hydroxide in 100 ml. of water for 24 hours. After the product was separated, washed free of alkali, dried and recrystallized, the refractive index was not appreciably different from that of the esterified cinnam.

Another portion of the esterified ether $\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{CO}_2\text{Na}$ was refluxed with excess powdered potassium hydroxide until all evidence of reaction had ceased, then filtered from the solids. The product was $\text{C}_6\text{H}_5\text{OC}_6\text{H}_3\text{CO}_2\text{Na}$, $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$, d_4^{25} 1.0297, 100% (theoretical) 100.4 (obs.) 100.6, η_0^{25} 1.0332.

Isomerization of Phenylcinnamate

To establish the structure of the cyclohexylideneether, the following reactions were recorded out.



One hundred five grams (0.5 mole) of cyclohexylidene was added with 100 grams (1.0 mole) of anhydrous zinc (96%) to a three neck glass flask equipped with stirrer and reflux condenser. The mixture was heated with stirring in a steam bath for 45 minutes, cooled to room temperature, 50 ml. of ethyl alcohol (absolute) added and refluxed for 15 minutes. The reaction mixture was then poured into a beaker of crushed ice, the lower layer separated and washed with cold sodium hydroxide solution, with water until alkali free, and dried over calcium sulfate. Fractionation gave 11 grams of cyclohexylidene, b.p. 130-131°, η_D^{20} 1.1931, d_4^{20} 1.005. These data are in agreement with those published for ethyl cyclohexylbenzoate and confirm the assumption that the structure of the original ether involves a phenoxy group attached to the carbon bearing the titanium atom.

Summary

- I. A number of alkylallylphenoxides and allylaryloxyethanes have been prepared by addition of alkoxide to fluorinated I_ns.
- II. A number of alkylallylphenoxides have been prepared by the addition of phenol and anisole to fluorinated I_ns, one of these was dehydrofluorinated to produce the corresponding unsaturated ethers.
- III. Alkylallylphenoxides of the types $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{X}$ and $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{X}$ have been shown to react further with alkoxide in the presence of aluminum I_n, to give polyalkoxy compounds of the etherether type.
- IV. Thermal decomposition of the ethers formed from highly branched alkoxide has been studied and the fragmentation identified.
- V. A mechanism has been proposed for the thermal decomposition of ethers formed by addition of secondary and tertiary alcohols to fluorinated I_ns.

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Berry G. Brown, III, was born at Durbin, Florida on March 7, 1919.

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COMMITTEE REPORT

This dissertation was prepared under the direction of
the Chairman of the candidate's Supervisory Committee and has
been approved by all members of the Committee. It was sub-
mitted to the Graduate Council and was approved as partial
fulfillment of the requirements for the degree of Doctor of
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